

## SPECTROPHOTOMETRIC STUDIES OF THERMODYNAMIC BASICITIES AND LANTHANIDES BINDING CONSTANTS OF LUMINESCENT COMPLEXES WITH BIPYRIDINE-TYPE LIGANDS

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The environment receives industrial emissions (1,2), which thereby affect the distribution of rare earth elements (REE) in the coastal waters (3). However, seawater contains REE at low concentrations (4), and it is necessary to study the REE fate in biogeochemical cycles of the marine environment (5). Low ion concentrations are difficult to measure in seawater (6,7). At the present time exists several methods of concentrating the dilute solutions of the lanthanide by the formation of complexes with organic compounds. Our investigation is devoted to the study of stability constants for 2,2'-bipyridyl-6,6'-dicarboxamides – potential REE ions extragent - *Table 1* with trivalent lanthanides.

*Table 1: Structure of the amide compounds.*

Abbreviation	R <sub>1</sub>	R <sub>2</sub>	Structure
(2,4,5-CH <sub>3</sub> )	Et	(2,4,5-CH <sub>3</sub> )ph	
(2,4-CH <sub>3</sub> )	Et	(2,4-CH <sub>3</sub> )ph	
(2,5-CH <sub>3</sub> )	Et	(2,5-CH <sub>3</sub> )ph	
(4-tBu)	Et	(4-tBu)ph	
(2-F)	Et	(2-F)ph	
(3-F)	Et	(3-F)ph	
(4-F)	Et	(4-F)ph	
(2-OOCH <sub>3</sub> )	Et	(2-OOCH <sub>3</sub> )ph	
(4-NO <sub>2</sub> )	Et	(4-NO <sub>2</sub> )ph	
(n-Oct)	(n-Oct)	(n-Oct)	

We selected these compounds as a good combination of chemical stability and easy accessibility. As a main goal we determine the stability constants of the complexes of REE ions as a thermodynamic value, which characterizes the strength of the complex in the solution. As example consider the constants for gadolinium(III) nitrate with various ligands *Figure 2*. *Figure 2* shows stability constants with an enhance of the electron withdrawing properties of the substituents at the diamide moiety. The highest stability were observed for gadolinium complexes of (4-F)Ph and (2,4,5-CH<sub>3</sub>)Ph ligands. The stability constants shows the following trend: (n-Oct)-ph < (4-NO<sub>2</sub>) < (2,4-CH<sub>3</sub>) < (2,5-CH<sub>3</sub>) < (3-F) < (2-OOCH<sub>3</sub>) < (2-F) < (4-tBu) < (2,4,5-CH<sub>3</sub>) < (4-F). In the case of *para*-fluorinated anilidic diamide the stability constants are the highest of the studied compounds. The methylation of the ligands results in a sharp stability increase of the complex with trimethylated anilidic moiety against of dimethylated ones, i.e. as much is the positive inductive effect of the substituent as stronger are the complexes with the ligand.

The major results of the investigation are:

1. all of the studied complexes possess 1:1 metal to ligand ratio;
2. the stability of the complexes of the heterocyclic diamides with all of the lanthanides are very strong with the logarithm of the stability constants higher than 5.3 for all of the systems under the study;
3. the stability constants are strongly depends on the nature of the substituent in diamide moiety;
4. the best affinity to the lanthanides shows the fluorinated ligand.

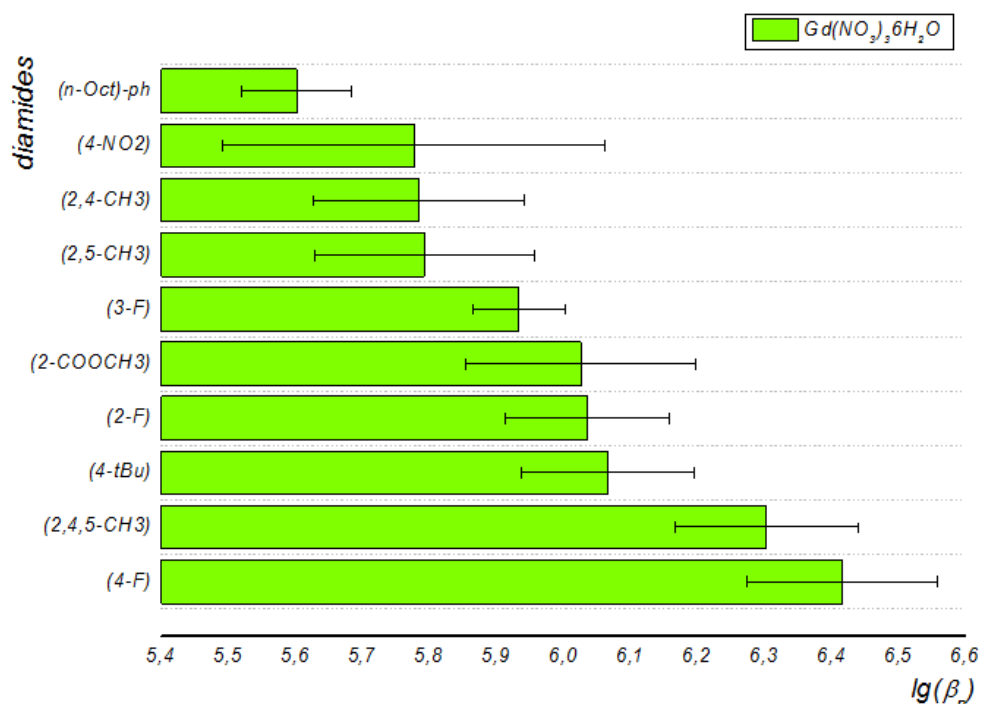


Figure 2: The spectrophotometric titration stability constants of complexes of diamides with neodymium nitrate in  $CH_3CN_{abs}$ .

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